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(54) Title: DYE TRANSFER INHIBITING COMPOSITIONS WITH SPECIFICALLY SELECTED METALLO CATALYSTS (57) Abstract The present invention relates to inhibiting dye transfer compositions comprising (i) one or more of a specific metallo catalyst selected from the group of porphyrins and/or phthalocyanines, (ii) an efficient amount of bleaching agent.		

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DYE TRANSFER INHIBITING COMPOSITIONS
WITH SPECIFICALLY SELECTED
METALLO CATALYSTS

Field of the Invention

The present invention relates to a composition and a process for inhibiting dye transfer between fabrics during washing. More in particular, the present invention relates to a composition and a process for inhibiting dye transfer between fabrics during washing comprising specifically selected metallo catalysts.

Background of the Invention

One of the most persistent and troublesome problems arising during modern fabric laundering operations is the tendency of some colored fabrics to release dye into the laundering solutions. The dye is then transferred onto other fabrics being washed therewith.

One way of overcoming this problem would be to bleach the fugitive dyes washed out of dyed fabrics before they have the opportunity to become attached to other articles in the wash.

Suspended or solubilized dyes can to some degree be oxidized in solution by employing known bleaching agents.

However it is important at the same time not to bleach the dyes actually remaining on the fabrics, that is, not to cause color damage.

U.S. Patent 4,077,768 describes a process for inhibiting dye transfer by the use of an oxidizing bleaching agent together with a catalytic compound such as iron porphins.

Copending EP Patent Application 91202655.6 filed October 9, 1991, relates to dye transfer inhibiting compositions comprising an enzymatic system capable of generating hydrogen peroxide and porphin catalysts.

It has now been found that specifically selected metallo catalysts in the presence of an efficient amount of a quick releasing bleaching agent are very efficient in preventing dye transfer.

Accordingly, a dye transfer inhibiting composition is provided which exhibits optimum dye transfer inhibiting properties.

According to another embodiment, the invention provides an efficient process for laundering operations involving colored fabrics.

Summary of the Invention

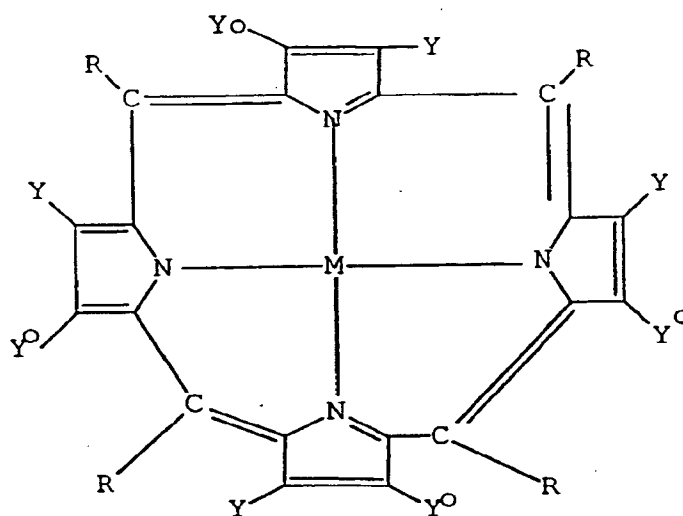
The present invention relates to inhibiting dye transfer compositions comprising

- i) one or more of a specific metallo catalyst selected from the group of porphyrins and/or phthalocyanines,
- ii) an efficient amount of bleaching agent.

Detailed description of the Invention

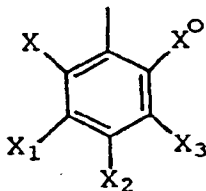
The term "specific metallo catalysts" herein encompasses one or more of a specific metallo catalyst selected from the groups of porphyrins and/or phthalocyanines as defined below.

A) porphyrins having the following formula I :



FORMULA I

wherein M is a transition metal capable of sustaining oxidation, and if desired may also be joined to one or more axial ligands in addition to the four nitrogen groups, each Y and Y° is independently H, fluoro or chloro, each R ring is



X and X° are independently H or an electronegative group which is not a water solubilizing group, eg. X and X° are independently, fluoro, chloro, bromo, or NO₂, X₁, X₂ and X₃ are independently H or an electronegative group, including water solubilizing electronegative groups, including without limitation fluoro, chloro, bromo, SO₃H, COCH or NO₂, subject to the provisions that

- 1) when none of X₁, X₂ and X₃ is not a water solubilizing group, then at least one Y and Y° on each porphyrin ring is other than H,
- 2) when Y and Y° are both H, at least one but not more than two of X₁, X₂ and X₃ is a water solubilizing group, eg. SO₃H or COOH, and at least two of X and X° and the X₁, X₂ and X₃ which are not a water solubilizing group are independently an electronegative group which is not a water solubilizing group, e.g. fluoro, chloro, bromo or NO₂, and
- 3) no more than two of X₁, X₂ and X₃ are water solubilizing groups, or the water soluble salts thereof in which said water solubilizing groups are in corresponding water soluble salt form.

Particular subgroups of the compounds of the formula I are the compounds of the formulae Ia and Ib.

The compounds of the formula Ia are those with reference to the structural formula I in which :

- a) at least one of Y and Y° on each porphyrin ring is fluoro or chloro and the other is H, fluoro or chloro,
- b) X and X° are independently H, fluoro, chloro, bromo or NO₂,
- c) X₁, X₂ and X₃ are independently H, fluoro, chloro, bromo, SO₃H, COOH or NO₂, provided that no more than two of X₁, X₂ and X₃ are SO₃H or COOH, and
- d) M is as above defined.

The compounds of the formula Ib are those with reference to the structural formula I in which

- a) Y and Y° are independently H, fluoro or chloro,
- b) X and X° are independently H, fluoro, chloro, bromo or NO₂,
- c) X₁, X₂ and X₃ are independently H, fluoro, chloro, bromo, SO₃H, COOH and NO₂ with the provisions that i) at least one but not more than two of X₁, X₂ and X₃ are SO₃H or COOH, and ii) at least two of X, X°, X₁, X₂ and X₃ is fluoro, chloro, bromo or NO₂, and
- d) M is as above defined.

The preferred compounds of the formula Ia have one or more of the following features :

- a) both Y and Y° on each porphyrin ring is fluoro or chloro;
- b) at least two of X, X°, X₁, X₂ and X₃ are fluoro or chloro, more particularly with X and X° being fluoro or chloro, and
- c) M is Fe, Cr, Mn, Co, Ru, Rh, Mo, V.

More preferred compounds of the formula Ia have one or more of the following features :

- a) both Y and Y° on each porphyrin ring is chloro;
- b) at least two of X, X°, X₁, X₂ and X₃ are chloro, more particularly with X and X° being chloro, and
- c) M is Fe, Mn.

The preferred compounds of the formula Ib have one or more of the following features :

- a) Y and Y° on each porphyrin ring is independently H or chloro;
- b) one of X₁, X₂ and X₃ is SO₃H,
- c) at least two of X, X°, X₁, X₂ and X₃ are fluoro or chloro, and
- d) M is Fe, Cr, Mn, Co, Ru, Rh, Mo, V.

More preferred compounds of the formula Ib have one or more of the following features :

- a) Y and Y° on each porphyrin ring are independently H or chloro,
- b) one of X₁, X₂ and X₃ is SO₃H,
- c) at least two of X, X°, X₁, X₂ and X₃ are chloro, more particularly with X and X° being chloro, and
- d) M is Mn, Fe.

Another preferred subclass of the compounds of the formula Ib are those in which one of Y and Y° on each porphyrin is other than H, more particularly those in which both Y and Y° are fluoro or chloro.

With regard to each R ring as described above, each R ring will contain the minimum substitution provided for above, but the positioning and number of substitutions above the minimum on each R ring may vary. Preferably, each R ring is the same.

In general, it is preferred that only one of X₁, X₂ and X₃ is a water solubilizing group. It is also more particularly preferred that when one of Y or Y° is to be other than H, that both be other than H.

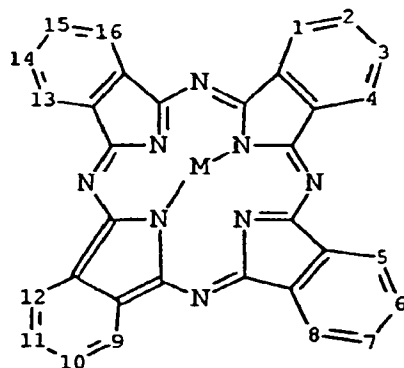
A subclass of the compounds of the formula Ib described in application Serial No. 039,566 of April 17, 1987, in which Y and Y° are H, X and X° are each chloro, X₁ and X₂ are H and R₃ is an electronegative group including a water solubilizing group is in free acid form and those with and without ligands such as the chloride ligand form.

The compounds of the invention having SO₃H or COOH groups are water soluble and the invention also includes such water soluble compounds in which such groups are in water soluble salt form with a cation of a base such as an alkali metal (sodium, potassium or lithium), and alkaline earth metal, or an ammonium cation, preferably an alkali metal or

ammonium cation. Such salt forms may be prepared by reacting a compound of the formula I with a base by conventional procedures.

M may be any transition metal which is capable of sustaining oxidation. Examples of preferred metals include Fe, Cr, Mn, V, Rh, Ru and Co. Particularly preferred metals are Fe and Mn. Additionally the metal may be joined to a ligand, The axial ligands, usually one or two but occasionally more, may be virtually any group which is capable of forming a single hydrolysable bond with the M, as known in the art. Examples of axial ligands by way of illustration only include $-OCH_3$, $-OH$, amines, halide ions, particularly chloride, and water.

B) Substituted phthalocyanines in which at least one of the peripheral carbon atoms in the 1-16 positions of the phthalocyanine nucleus (M Pc), as shown in Formula (1) :



Formula (1)

wherein M is selected from Fe, Cr, Mn, Co, Ru, Rh, Mo, V

are unsubstituted or substituted by any combination of atoms or groups and sulphonated derivatives thereof provide that the phthalocyanine absorbs electromagnetic radiation at a wavelength from 650nm to 800nm.

In the present phthalocyanines the phthalocyanine nucleus is complexed with a metal represented by M. Preferred metals represented by M are Fe, Mn, Co, Rh, Cr, Ru, Mo or V.

In the phthalocyanines used in the present invention each of the pendant organic radicals linked via oxygen to the phthalocyanine nucleus is independently selected from aromatic, heteroaromatic, aliphatic and alicyclic radicals, such that any one phthalocyanine nucleus may carry two or more different organic radicals.

It is preferred that each pendant organic radical is independently selected from mono- and bi-cyclic aromatic and heteroaromatic radicals.

Examples of suitable mono- and bi-cyclic aromatic and heteroaromatic radicals are phenyl, naphthyl, especially naphth-2-yl, pyridyl, thiophenyl, furanyl, quinolinyl, thiazolyl, benzothiazolyl and pyrimidyl each of which may be substituted.

Where the pendant organic radical is an aliphatic or alicyclic radical it is preferred that it is selected from C₁-20-alkyl especially C₁-10 alkyl; C₂-20 alkenyl especially C₃-10 alkenyl and C₄-8 cycloalkyl especially cyclohexyl, each of which may be substituted.

Optional substituents for the pendant organic radicals are preferably selected from C₁-20 alkyl, especially C₁-4 alkyl; C₁-20 alkoxy, especially C₁-4 alkoxy, C₁-20 alkenyl, especially C₂-4 alkenyl; C₁-20 alkylthio, especially C₁-4 alkylthio; C₁-20 alkoxycarbonyl, especially C₁-4 alkoxycarbonyl; hydroxyC₁-4 alkoxy, aryl, especially phenyl; C₁-4 alkylaryl, especially benzyl; arylthio, especially phenylthio; halogen, especially fluoro, chloro and bromo; -CN; -NO₂; -CF₃; -COR²; -COOR²; -CONR²R³, -SO₂R², -SO₂NR²R³ and -OR² in which R² and R³ are independently selected from -H; alkyl, especially C₁-4 alkyl; aryl, especially phenyl; C₁-4 alkylaryl, especially benzyl and -SO₃A in which A is H, or a metal or ammonium ion or substituted ammonium ion.

In the phthalocyanines used in the present invention it is preferred that from 4 to 16 of the peripheral carbon atoms are linked via an oxygen atom to a pendant organic radical and it is especially preferred that all 16 peripheral carbon atoms are linked via an oxygen atom to a pendant organic radical.

Examples of suitable atoms or groups which can be attached to any of the remaining peripheral carbon atoms of the phthalocyanine nucleus are hydrogen, halogen, sulphonate groups $-\text{SO}_3\text{A}$ in which A is H, or a metal or ammonium ion or a substituted ammonium ion, and any of the pendant organic radicals described above and hereinafter represented by R. It is preferred that the atoms or groups attached to the remaining peripheral carbon atoms are selected from $-\text{H}$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{SO}_3\text{H}$, $-\text{SO}_3\text{Na}$, $-\text{SO}_3\text{K}$, $-\text{SO}_3\text{Li}$ and $-\text{SO}_3\text{NH}_4$ or any combination thereof. It is especially preferred that these atoms or groups are $-\text{H}$, $-\text{Cl}$, $-\text{Br}$, $-\text{SO}_3\text{H}$, $-\text{SO}_3\text{Na}$ or $-\text{SO}_3\text{NH}_4$.

The sulphonated derivatives of the phthalocyanines used in the present invention carrying up to 50 SO_3A groups, preferably up to 40 SO_3A groups and more preferably up to 30 SO_3A groups, which are attached directly to the phthalocyanine nucleus and/or to the pendant organic radicals are a preferred group of compounds for the present invention.

In the preferred group the average number of SO_3A groups is preferably from 2 to 40 and more preferably from 2 to 30 and especially, preferably 16 to 30. It is also preferred that for each pendant organic radical there is at least one SO_3A group, although each organic radical may carry none, one or more than one SO_3A group.

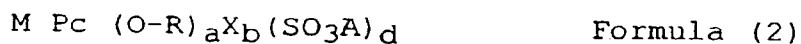
Where A is a metal ion it is preferably an alkali or alkaline earth metal ion, especially an alkali metal ion such as a sodium, potassium or lithium ion. Where A is an ammonium ion it is preferably $^+\text{NH}_4$ or a substituted ammonium ion which enhances the water-solubility of the compound. Examples of suitable substituted ammonium ions which enhance the water solubility of the compound are mono, di, tri and tetra alkyl and hydroxylalkyl ammonium ions in which the alkyl groups preferably contain from 1 to 4 carbon atoms such as $^+\text{N}(\text{CH}_3)_4$; $^+\text{N}(\text{C}_2\text{H}_5)_4$; $^+\text{N}(\text{C}_2\text{H}_4\text{OH})_4$; $^+\text{NH}_3\text{CH}_3$; $^+\text{NH}_2(\text{CH}_3)_2$ and $^+\text{NH}(\text{CH}_3)_3$.

The substituted ammonium ion represented by A preferably has one fatty alkyl group as described above, the remaining groups being preferably H or C_{1-4} alkyl, especially H or methyl. Suitable ammonium ions include 2-

ethylhexylammonium, 1,1,3,3-tetramethylbutylammonium and 3,5,5-trimethylhexylammonium.

In compounds of the Formula (1) each of the peripheral carbon atoms in the 1 to 16 positions of the phthalocyanine nucleus are attached to a group Y and each Y is independently selected from -H, halogen, -SO₃A in which A is as hereinbefore defined, and OR in which R is a pendant organic radical as hereinbefore defined.

According to a further feature of the present invention there are provided phthalocyanine compounds of the Formula (2) :



wherein :

M Pc is a phthalocyanine nucleus as defined in Formula (1);
each R independently is an organic radical;
each X independently is a halogen or hydrogen; the O-R and X groups being attached to one or more of the 16 peripheral carbon atoms of the phthalocyanine nucleus;

A is selected from H, a metal, ammonium or substituted ammonium as described above;

a is from 1 to 16;

b is from 0 to 15;

d is an average value from 0.1 to 50;

a+b is from 1 to 16;

In phthalocyanines of Formula (2) M is any of the metals described above for M.

In phthalocyanines for Formula (2) it is especially preferred that M is Fe, Mn.

In a phthalocyanine of Formula (2) each of the radicals denoted by R may be selected from any of the pendant organic radicals hereinbefore defined in relation to Formula (1) above.

In a phthalocyanine of formula (2) it is preferred that a is from 4 to 16 and more preferably from 5 to 16. It is especially preferred that a is 16.

In a phthalocyanine of Formula (2) each halogen denoted by X is preferably independently selected from -F, -Cl, -Br

and -I and it is especially preferred that each halogen denoted by X is independently -Cl or -Br.

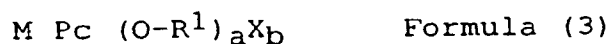
In a phthalocyanine of Formula (2) it is preferred that b is from 0 to 12, and more preferably from 0 to 11.

When a+b is <16 the remainder of the 16 peripheral carbon atoms, not carrying a group O-R or X, may carry a sulphonate group, -SO₃A or a group represented by R. It is however preferred that the sum of a+b is 16. It is also preferred that a is 4, 8, 12 or 16, and especially 8, 12 or 16.

In phthalocyanines of Formula (2) the metal ion denoted by A is preferably an alkali or alkaline earth metal ion and more preferably is selected from lithium, sodium and potassium ion. It is especially preferred that a is a sodium, an ammonium ion or hydrogen.

In phthalocyanines of Formula (2) it is preferred that d is an average value from 2 to 40. It is more preferred that d is an average value from 2 to 30, especially preferred that d is an average value from 16 to 30.

According to a further feature of the present invention there are provided phthalocyanine compounds of the Formula (3):



wherein :

M Pc is as defined in Formula (1)

R¹ is selected from optionally substituted aryl and optionally substituted heteroaryl;

X is halogen or H;

a is an integer from 1 to 16;

b is an integer from 0 to 15; and

a+b is equal to 16.

Preferred phthalocyanine compounds of formulae (3) are those (1) wherein :

M is selected from Mn, Fe, Co;

X is halogen;

a is 4, 8 or 12; and b is 12, 8 or 4.

- (2) wherein :
M is selected from Mn, Fe, Co, V;
X is halogen;
a is 4, 8 or 12 and b is 12, 8, 4.
- (3) wherein :
M is selected from Mn, Fe;
X is hydrogen;
a is 8 or 12; and b is 8 or 4.
- (4) wherein :
M is selected from Fe, Mn, Ni;
a is from 5 to 16; and b is from 11 to 0.
- (5) wherein :
M is selected from Fe, Mn, Ni;
a is from 1 to 3, and b is from 15 to 3.
- (6) wherein :
M is selected from Fe, Mn, Co, Ni and V;
X is halogen;
a is from 1 to 16; and b is from 15 to 0.
- (7) wherein :
M is selected from Fe, Mn, Co, Ni and V;
a is from 1 to 14; and b is from 15 to 2, provided that
at least one X is H and one X is halogen.

In a phthalocyanine of Formula (3) it is preferred that each of the radicals denoted by R^1 is independently selected from mono- or bi-cyclic aromatic or heteroaromatic radicals. Examples of suitable aromatic and heteroaromatic radicals are those described above for R. The radicals denoted by R^1 are more preferably phenyl or naphthyl, especially 2-naphthyl. Preferred substituents for the R^1 group are as described for R.

In a phthalocyanine of Formula (3) it is preferred that a is an integer from 4 to 16 and that b is an integer from 12 to 0. It is also preferred that a is 4, 8, 12 or 16, more especially 8, 12 or 16, and that b is 12, 8, 4 or 0.

In a phthalocyanine of Formula (3) it is preferred that the metal denoted by M is Fe, Mn, Co, Cr, Ru, Rh, Mo, V.

The phthalocyanines can be sulphonated directly on the Pc nucleus, particularly when any of the 1-16 positions is unsubstituted (i.e. the 1-16 peripheral carbon atoms carry a hydrogen atom) or on any of the pendant organic groups R or R¹, or on both the Pc nucleus and the pendant organic groups.

The preferred molar range of the specifically selected metallo catalyst of the present invention in the wash is 10⁻⁸ molar to 10⁻³ molar, more preferably 10⁻⁶ to 10⁻⁴ molar.

An efficient amount of bleaching agent

The dye transfer inhibiting compositions according to the present invention comprise an efficient amount of bleaching agent.

According to the present invention, an efficient amount of bleach is by definition the necessary amount of bleach which combined with a bleach catalyst leads to a level of dye oxidation which is between 40% to 100%, preferably 40% to 60%, more preferred 60% to 80%, most preferred 80%-100% of the maximum (Z) per cent of dye oxidation that can be achieved under the most optimal conditions determined by those skilled in the art.

The bleaches suitable for the present invention can be activated or non-activated bleaches.

Preferably, the bleaches suitable for the present invention include peroxygen bleaches. Examples of suitable water-soluble solid peroxygen bleaches include hydrogen peroxide releasing agents such as hydrogen peroxide, perborates, e.g. perborate monohydrate, perborate tetrahydrate, persulfates, percarbonates, peroxydisulfates, perphosphates and peroxyhydrates. Preferred bleaches are percarbonates and perborates.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetylenediamine (TAED), nonanoyloxybenzenesulfonate (NOBS, described in US 4,412,934), 3,5,5-trimethylhexanoloxybenzenesulfonate (ISONOBS, described in EP 120,591), or pentaacetylglucose (PAG), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect.

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Other peroxygen bleaches suitable for the present invention include organic peroxyacids such as percarboxylic acids.

Test Methods:

For a given catalyst concentration, temperature and pH, the following two test methods can be used to estimate the optimum bleach level that gives the maximum level of dye oxidation, i.e. Z.

(a) In solution dye bleaching:

In a detergent solution, fix the initial concentration of dye (e.g. 40 ppm) and catalyst. Record the absorbance spectrum of this solution using a UV-Vis spectrophotometer according to procedures known to those skilled in the art. Add a given concentration of bleach (H₂O₂, oxone, percarbonate, perborate, activated bleach, etc..) and stir the solution containing the dye and catalyst. After stirring for 30 min, record again the absorbance spectrum of the solution. The amount of dye oxidation can then be determined from the change in the absorbance maximum for the dye. Keeping the experimental conditions the same, vary the amount of bleach so as to achieve the maximum dye oxidation.

(b) Reduction of dye transfer from fabric to another fabric

In either a washing machine or launderometer, add a known bleeding fabric and a known uncolored pick-up tracer (e.g. cotton) to the wash load. After simulating a wash cycle, determine the amount of dye that has been picked up by the tracer according to methods known to those skilled in the art. Now to separate washing machines, add the same amount of bleeding fabric and pick-up tracer, a fixed amount of catalyst and vary the bleach level. Determine the level of dye transfer onto the pick-up tracers and vary the amount of bleach as to minimize dye transfer. In this way the most optimal bleach concentration can be determined.

DETERGENT ADJUNCTS

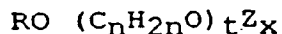
A wide range of surfactants can be used in the detergent compositions. A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in US Patent 3,664,961 issued to Norris on May 23, 1972.

Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulphonate and sulphate surfactants in a weight ratio of from 5:1 to 1:2, preferably from 3:1 to 2:3, more preferably from 3:1 to 1:1. Preferred sulphonates include alkyl benzene sulphonates having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid esters in which the fatty acid is derived from a C₁₂-C₁₈ fatty source preferably from a C₁₆-C₁₈ fatty source. In each instance the cation is an alkali metal, preferably sodium. Preferred sulphate surfactants are alkyl sulphates having from 12 to 18 carbon atoms in the alkyl radical, optionally in admixture with ethoxy sulphates having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6. Examples of preferred alkyl sulphates herein are tallow alkyl sulphate, coconut alkyl sulphate, and C₁₄-C₁₅ alkyl sulphates. The cation in each instance is again an alkali metal cation, preferably sodium.

One class of nonionic surfactants useful in the present invention are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 13.5, more preferably from 10 to 12.5. The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

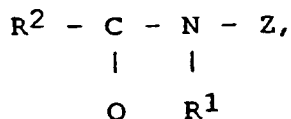
Especially preferred nonionic surfactants of this type are the C₉-C₁₅ primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C₁₄-C₁₅ primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol and the C₁₂-C₁₄ primary alcohols containing 3-5 moles of ethylene oxide per mole of alcohol.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula



wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent are disclosed in EP-B 0 070 077, 0 075 996 and 0 094 118.

Also suitable as nonionic surfactants are poly hydroxy fatty acid amide surfactants of the formula



wherein R^1 is H, or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative thereof. Preferably, R^1 is methyl, R^2 is a straight C_{11-15} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B or HS.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ($Na_2Si_2O_5$).

Suitable polycarboxylates builders for use herein include citric acid, preferably in the form of a water-soluble salt, derivatives of succinic acid of the formula $R-CH(COOH)CH_2(COOH)$ wherein R is C_{10-20} alkyl or alkenyl, preferably C_{12-16} , or wherein R can be substituted with hydroxyl, sulfo sulfoxyl or sulfone substituents. Specific examples include lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenylsuccinate, 2-tetradecenyl succinate. Succinate builders are preferably used in the form of their water-soluble salts, including sodium, potassium, ammonium and alkanolammonium salts.

Other suitable polycarboxylates are oxodisuccinates and mixtures of tartrate monosuccinic and tartrate disuccinic acid such as described in US 4,663,071.

Especially for the liquid execution herein, suitable fatty acid builders for use herein are saturated or unsaturated C10-18 fatty acids, as well as the corresponding soaps.

Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid.

Preferred builder systems for use in granular compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid.

Other builder materials that can form part of the builder system for use in granular compositions the purposes of the invention include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 10% to 80% by weight of the composition preferably from 20% to 70% and most usually from 30% to 60% by weight.

Other components used in detergent compositions may be employed, such as bleaches, suds boosting or depressing agents, enzymes and stabilizers or activators therefor, soil-suspending agents soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and perfumes.

Especially preferred are combinations with technologies which also provide a type of color care benefit. Examples of these technologies are polyvinylpyrrolidone polymers and other polymers which have dye transfer inhibiting properties. Another example of said technologies are cellulase for color maintenance/ rejuvenation.

Other examples are polymers disclosed in EP 92870017.8 filed January 31, 1992 and enzyme oxidation scavengers disclosed in EP 92870018.6 filed January 31, 1992. also particularly suitable are amine base catalyst stabilizers disclosed in EP 92870019.4 filed January 31, 1992.

The detergent compositions according to the invention can be in liquid, paste or granular forms. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l; in such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt. The liquid compositions according to the present invention can also be in "concentrated form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents.

The present invention also relates to a process for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

The process comprises contacting fabrics with a laundering solution as hereinbefore described.

The process of the invention is conveniently carried out in the course of the washing process. The washing process is preferably carried out at 5 °C to 75 °C, especially 20 to 60,

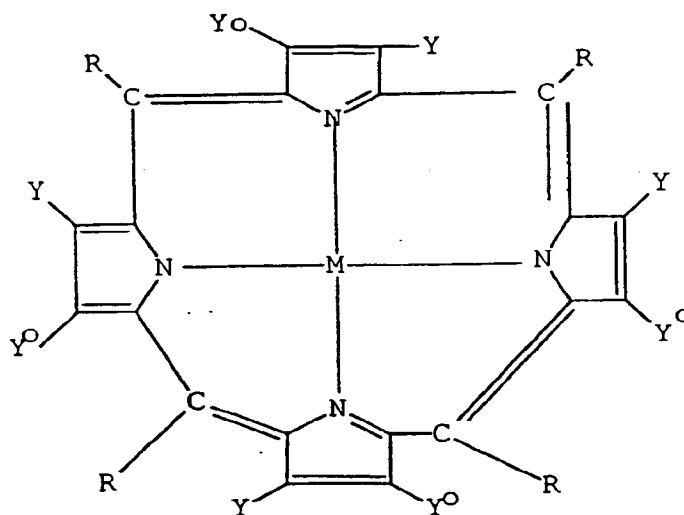
but the polymers are effective at up to 95 °C. The pH of the treatment solution is preferably from 7 to 11, especially from 7.5 to 10.5.

The process and compositions of the invention can also be used as additive during laundry operations.

WHAT IS CLAIMED IS:

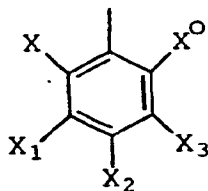
1. A dye transfer inhibiting composition comprising
 i) one or more of a specific metallo catalyst selected from
 the group of porphyrins and/or phthalocyanines,

said porphyrins having the formula I



FORMULA I

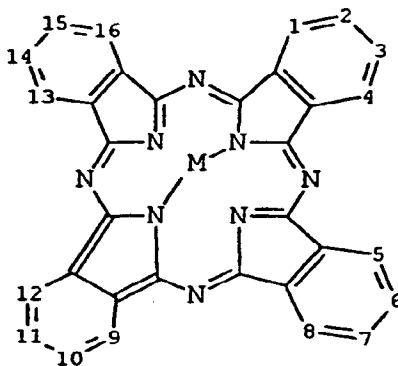
wherein M is a transition metal capable of sustaining oxidation, and if desired may also be joined to one or more axial ligands in addition to the four nitrogen groups, each Y and Y° is independently H, fluoro or chloro, each R ring is



X and X° are independently H or an electronegative group which is not a water solubilizing group, eg. X and X° are independently, fluoro, chloro, bromo, or NO₂, X₁, X₂ and X₃ are independently H or an electronegative group, including water solubilizing electronegative groups, including without limitation fluoro, chloro, bromo, SO₃H, COCH or NO₂, subject to the provisions that

- 1) when none of X₁, X₂ and X₃ is not a water solubilizing group, then at least one Y and Y° on each porphyrin ring is other than H,
- 2) when Y and Y° are both H, at least one but not more than two of X₁, X₂ and X₃ is a water solubilizing group, eg. SO₃H or COOH, and at least two of X and X° and the X₁, X₂ and X₃ which are not a water solubilizing group are independently an electronegative group which is not a water solubilizing group, e.g. fluoro, chloro, bromo or NO₂, and
- 3) no more than two of X₁, X₂ and X₃ are water solubilizing groups, or the water soluble salts thereof in which said water solubilizing groups are in corresponding water soluble salt form,

said phthalocyanines having the formula (1)



Formula (1)

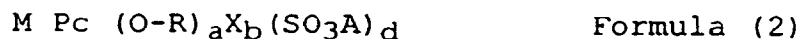
wherein M is selected from Fe, Cr, Mn, Co, Ru, Rh, Mo, V, in which at least one of the peripheral carbon atoms in the 1-16 positions of the phthalocyanine nucleus (M Pc) are unsubstituted or substituted by any combination of atoms or groups and sulphonated derivatives thereof provide that the phthalocyanine absorbs electromagnetic radiation at a wavelength from 650nm to 800nm,

ii) an efficient amount of bleaching agent.

2. A detergent inhibiting composition according to claim 1 wherein the porphyrins have one or more of the following features :

- a) Y and Y° on each porphyrin ring are independently H or chloro,
- b) one of X₁, X₂ and X₃ is SO₃H,
- c) at least two of X, X°, X₁, X₂ and X₃ are chloro, more particularly with X and X° being chloro, and
- d) M is Mn, Fe.

3. A detergent inhibiting composition according to claim 1 where the phthalocyanine have the formula (2)



wherein :

M Pc is a phthalocyanine nucleus as defined in Formula (1);
 each R independently is an organic radical;
 each X independently is a halogen or hydrogen; the O-R and X groups being attached to one or more of the 16 peripheral carbon atoms of the phthalocyanine nucleus;

A is selected from H, a metal, ammonium or substituted ammonium as described above;

a is from 1 to 16;

b is from 0 to 15;

d is an average value from 0.1 to 50;

a+b is from 1 to 16.

4. A detergent inhibiting composition according to claim 1 where the phthalocyanine have the formula (3)



wherein :

M Pc is as defined in Formula (1)

R¹ is selected from optionally substituted aryl and optionally substituted heteroaryl;

X is halogen or H;

a is an integer from 1 to 16;

b is an integer from 0 to 15; and

a+b is equal to 16.

5. A dye transfer inhibiting composition according to claims 1-4 wherein the wash concentration of the metallo catalyst is from 10⁻⁸ to 10⁻³ molar, preferably from 10⁻⁶ to 10⁻⁴ molar.
6. A dye transfer inhibiting composition according to claims 1-5 wherein the bleaching agent is selected from an activated or a non-activated bleach.
7. A dye transfer inhibiting composition according to claims 1-6 which is a detergent additive, in the form of a non-dusting granule or a liquid.
8. A detergent composition which comprises a dye transfer inhibiting composition according to any of the preceding claims further comprising enzymes, surfactants, builders, and other conventional detergent ingredients.
9. A detergent composition which comprises a dye transfer inhibiting composition according to any of the preceding claims further comprising a cellulase.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/05035

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C11D 3/28, 3/39, 3/395, 7/38, 7/32, 7/54; D06L 1/12, 3/02

US CL : 8/111, 137; 252/1, 102, 186.43, 524, 542

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 8/111, 137; 252/1, 102, 186.43, 524, 542

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,077,768 [JOHNSTON] 07 March 1978 See the claims.	1-5
A	US, A, 4,672,047 [CHANDLER] 09 June 1987	NONE
X	US, A, 4,892,941 [DOLPHIN] 09 January 1990 See EXAMPLES 11 and 16.	1-5
Y	EP, A, 0 306 089 [STEPHENSON] 08 March 1989 See the EXAMPLES and the claims.	1-5
Y	EP, A, 0 538 228 [THOEN] 21 April 1993 See the Examples and the claims.	1-5
Y,P	EP, A, 0 596 184 [FREDJ] 11 May 1994 See the EXAMPLES and the claims.	1-5

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A* document defining the general state of the art which is not considered to be of particular relevance	* X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* E* earlier document published on or after the international filing date	* Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* G*	document member of the same patent family
* O* document referring to an oral disclosure, use, exhibition or other means		
* P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

19 JULY 1995

Date of mailing of the international search report

09 AUG 1995

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/05035

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	EP, A, 0 622 447 [FREDJ] 02 November 1994 See the Examples and the claims.	1-5
X,P	WO, A, 94/24250 [PRAMOD] 27 October 1994 See Page 7, lines 1-18 and the claims.	1-5
Y,P	EP, A, 0 622 448 [DANY] 02 November 1994 See the Examples and the claims.	1-5

Form PCT/ISA/210 (continuation of second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/05035

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 6-9
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.